

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: TSUJI et al.  
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Examiner: Zimmer, Marc S.  
For: THERMOCONDUCTIVE ADDITION-CURABLE LIQUID  
SILICONE RUBBER COMPOSITION AND COATED FIXING  
ROLL

**STATEMENT OF ACCURACY OF ENGLISH TRANSLATION**

Dear Sir:

This statement is to certify that I am skilled in both the Japanese language and the English language. I have reviewed the translation of Japanese Patent Application No. 2003-110557 included herewith. I certify that this translation is accurate.

A handwritten signature in cursive script, reading "Hiroyuki Yamada", is written over a horizontal line.

Hiroyuki Yamada

[Document Designation]	Specification
[Title of the Invention]	THERMOCONDUCTIVE ADDITION-CURABLE LIQUID SILICONE RUBBER COMPOSITION

[Claims]

[Claim 1] A thermoconductive addition-curable liquid silicone rubber composition having a thermal conductivity of at least 0.3 W/(m·K) after curing which comprises

- (A) 100 parts by weight of liquid diorganopolysiloxane that has a viscosity of 100 to 100,000 mPa·s and contains at least two silicon-bonded alkenyl groups in each molecule,
- (B) 50 to 400 parts by weight of alumina micropowder that has an average particle size of 0.1 to 50  $\mu\text{m}$ ,
- (C) 20 to 100 parts by weight of iron oxide micropowder that has an average particle size of 0.01 to 0.5  $\mu\text{m}$ ,
- (D) 0.1 to 2.0 parts by weight of cerium oxide micropowder, cerium hydroxide micropowder, or cerium-containing heteroorganosiloxane,
- (E) organopolysiloxane that contains at least two silicon-bonded hydrogen atoms in each molecule, wherein the component (E) content provides from 0.3 to 5 moles silicon-bonded hydrogen atom in component (E) per 1 mole silicon-bonded alkenyl in component (A), and
- (F) platinum catalyst in a catalytic quantity.

[Claim 2] The thermoconductive addition-curable liquid silicone rubber composition in accordance with claim 1 characterized in that the surface of the alumina micropowder (B) has been treated with a surface treatment agent.

[Claim 3] The thermoconductive addition-curable liquid silicone rubber composition in accordance with claim 2 characterized in that the surface treatment agent is organoalkoxysilane, tetraalkoxysilane, or a partial hydrolysis and/or condensation product of tetraalkoxysilane.

[Claim 4] The thermoconductive addition-curable liquid silicone rubber composition in accordance with claim 1 characterized in that component (C) is in the form of a paste afforded by preliminary microdispersion in a portion of component (A).

[Claim 5] The thermoconductive addition-curable liquid silicone rubber composition in accordance with claim 1 that characteristically is for use as a silicone rubber in a heat fixing rolls having a silicone rubber layer in which the surface of the silicone rubber layer is coated with a fluoro-resin or a fluororubber.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to a thermoconductive addition-curable liquid silicone rubber composition. More particularly, this invention relates to a thermoconductive addition-curable liquid silicone rubber composition that exhibits excellent adherence to substrate in contact with the composition during its cure and that after curing exhibits a fully satisfactory strength and high thermal conductivity and does not exhibit changes in these properties even during long-term heating.

[0002]

[Back Ground of the Invention]

Silicone rubber has been used in the heat fixing rolls employed in, for example, electrophotographic copiers, electronic printers, and facsimile machines. Silicone rubber has been used in this application because its heat resistance is superior to that of other rubbers.

The addition-curable silicone rubber compositions used in heat fixing rolls have mainly been compositions that contain crystalline silica, for example, quartz powder. For example, Japanese Unexamined Laid Open Patent Application Publication Number (hereinafter referred to as Kokai) Hei 5-297747 teaches a silicone rubber composition that is used for heat fixing silicone rubber rollers. This composition contains quartz powder and iron oxide. Kokai Hei 10-222558 teaches an addition-curable liquid silicone rubber composition for fluororesin-coated fixing rolls; this composition contains iron oxide having a particular particle size and crystalline silica. The addition-curable silicone rubber composition for fluororesin- or fluorol latex-coated silicone rubber fixing rolls disclosed in Kokai Hei 11-60955 contains filler, cerium oxide, and iron oxide.

[0003]

Silicone rubbers with high thermal conductivities have been used in recent years in response to faster printing speeds and shorter machine warm-up times. However, various problems occur when the content of crystalline silica or prior-art filler in the above-described silicone rubber compositions is increased in pursuit of improved thermal conductivities. These problems include failure to obtain an adequate improvement in the thermal conductivity and, with respect to long-term use under heating, an inability to exhibit a stable performance due to changes in such physical properties as hardness, a reduction in adherence to the metal core, and/or shortening of the device life.

[0004]

This has led to the use of thermoconductive liquid silicone rubber compositions loaded with large amounts of thermoconductive filler. As compared to the crystalline silica and prior-art fillers referenced above, thermoconductive fillers exhibit excellent thermal conductivities at relatively low fill levels. Thermoconductive liquid silicone rubber compositions loaded with large amounts of alumina micropowder are disclosed in, for example, Kokai Hei 9-12893, Kokai Hei 10-39666, Kokai Hei 11-116806, Kokai Hei 11-158383, and Kokai 2002-72728.

[0005]

However, for these silicone rubber compositions as well, it has been found that, depending on the particular conditions of use, the problems of impaired adhesion to the metal core and unstable physical properties (e.g., hardness) during long-term use under heating still occur. For example, during application as the covering for rolls that undergo high-speed rotation at high roll-to-roll pressures while heated, the silicone rubber layer will rupture or peel — either initially or after long-term use in a heated state — due to inadequate strength by the cured material. Reinforcing fillers such as finely divided silica are typically used to improve the strength of cured silicone rubber. However, there are limits on their levels of addition since the addition of such reinforcing fillers to a thermoconductive liquid silicone rubber composition containing large amounts of thermoconductive filler results in a substantial increase in the pre-cure viscosity, with

has a negative effect on the injectability and workability. In the end, then, one has been left with the problems of an inadequate reinforcement and a distinct tendency for the physical properties to change during long-term use under heating.

[0006]

[Patent Reference 1]

Kokai Hei 5-297747

[Patent Reference 2]

Kokai Hei 11-222558

[Patent Reference 3]

Kokai Hei 11-60955

[Patent Reference 4]

Kokai Hei 9-12893

[Patent Reference 5]

Kokai Hei 10-39666

[Patent Reference 6]

Kokai Hei 11-116806

[Patent Reference 7]

Kokai Hei 11-158383

[Patent Reference 8]

Kokai 2002-72728

[0007]

[Problems to Be Solved by the Invention]

The object of this invention is to provide a thermoconductive liquid silicone rubber composition that exhibits excellent adherence to substrate in contact with the composition during its cure and that after curing exhibits a fully satisfactory strength and high thermal conductivity and does not exhibit changes in these properties even when subjected to long-term heating.

[0008]

[Means Solving the Problems]

The inventors achieved this invention as a result of intensive investigations into the problems described above. More specifically, the thermoconductive addition-curable liquid silicone rubber composition according to this invention characteristically has a thermal conductivity of at least 0.3 W/(m·K) after curing and comprises

- (A) 100 parts by weight of liquid diorganopolysiloxane that has a viscosity of 100 to 100,000 mPa·s and contains at least two silicon-bonded alkenyl groups in each molecule,
- (B) 50 to 400 parts by weight of alumina micropowder that has an average particle size of 0.1 to 50  $\mu\text{m}$ ,
- (C) 20 to 100 parts by weight of iron oxide micropowder that has an average particle size of 0.01 to 0.5  $\mu\text{m}$ ,
- (D) 0.1 to 2.0 parts by weight of cerium oxide micropowder, cerium hydroxide micropowder, or cerium-containing heteroorganosiloxane,

- (E) organopolysiloxane that contains at least two silicon-bonded hydrogen atoms in each molecule, wherein the component (E) content provides from 0.3 to 5 moles silicon-bonded hydrogen atom in component (E) per 1 mole silicon-bonded alkenyl in component (A), and
- (F) platinum catalyst in a catalytic quantity.

[0009]

[Best Mode for Carrying out The Invention]

This invention is described in detail hereinbelow.

The liquid diorganopolysiloxane (A) has a viscosity of 100 to 100,000 mPa·s and contains at least two silicon-bonded alkenyl groups in each molecule. This liquid diorganopolysiloxane is the main component for generating a rubber upon the crosslinking of the composition according to the present invention. The subject diorganopolysiloxane is represented by the average unit formula  $R_nSiO_{(4-n)/2}$  wherein the subscript  $n$  is 1.9 to 2.1 and R is alkyl such as methyl, ethyl, propyl, butyl, pentyl, and hexyl; alkenyl such as vinyl, allyl, propenyl, butenyl, pentenyl, hexenyl, and heptenyl; aryl such as phenyl, tolyl, and xylyl; aralkyl such as benzyl and phenethyl; or halogen-substituted monovalent hydrocarbyl such as 3-chloropropyl and 3,3,3-trifluoropropyl. The molecular structure of component (A) is specifically straight chain or partially branched straight chain and preferably is straight chain. The alkenyl content in R for this diorganopolysiloxane is generally 0.01 to 5 mole%. The diorganopolysiloxane under consideration is exemplified by

trimethylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane copolymers,

trimethylsiloxy-endblocked methylvinylpolysiloxanes,

trimethylsiloxy-endblocked methylvinylsiloxane-methylphenylsiloxane copolymers,

trimethylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane-methylphenylsiloxane copolymers,

dimethylvinylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane copolymers,

dimethylvinylsiloxy-endblocked methylvinylpolysiloxanes,

dimethylvinylsiloxy-endblocked methylvinylsiloxane-methylphenylsiloxane copolymers,

dimethylvinylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane-methylphenylsiloxane copolymers,

dimethylvinylsiloxy-endblocked dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers, and

dimethylvinylsiloxy-endblocked dimethylsiloxane-methylvinylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers.

[0010]

The alumina micropowder (B) functions to improve the post-cure thermal conductivity of the inventive composition.

The shape of component (B) is not critical and this component may be spherical or irregular. The average particle size of component (B) is in the range of 0.1 to 50  $\mu\text{m}$ , and is preferably in the range of 0.1 to 10  $\mu\text{m}$  in order to prevent sedimentation of the alumina micropowder during long-term storage of the composition according to the present invention. In order for the inventive composition to provide a post-cure hardness that exhibits good stability with respect to heating, the ignition loss, as measured by the ignition loss method specified in Japanese

Industrial Standard (JIS) H 1901 (heating temperature = 1,100°C, heating time = 1 hour), is preferably no more than 0.15 weight%.

[0011]

The surface of the alumina micropowder (B) is preferably treated with a surface treatment agent because this facilitates mixing with component (A), prevents separation and sedimentation of component (B) from the inventive composition, and can reduce the viscosity of the inventive composition. The surface treatment agent may be exemplified by organoalkoxysilanes such as methyltrimethoxysilane, methyltriethoxysilane, vinyltrimethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxysilane, and n-octyltrimethoxysilane; tetraalkoxysilanes and their partial hydrolysis and condensation products, such as tetramethoxysilane, tetrapropoxysilane, and ethylpolysilicate; organohalosilanes such as dimethyldichlorosilane and methyltrichlorosilane; organosilazanes such as hexamethyldisilazane; organosilicon compounds such as dimethylhydroxysiloxy-endblocked diorganosiloxane oligomers and cyclopolydiorganosiloxanes; and amine compounds such as tri-n-butylamine and tri-n-octylamine. Organosilicon compounds are preferred among the preceding for their low cure inhibition, while organoalkoxysilanes and tetraalkoxysilanes and their partial hydrolysis and condensation products are particularly preferred from the standpoint of the ease of the surface treatment process. Surface treatment of the alumina micropowder (B) may be carried out, for example, by adding the surface treatment agent to component (B) and heating and stirring in a mixer, or by adding the surface treatment agent at the same time component (B) is added to component (A) and heating and stirring with a mixer. While the amount addition of the surface treatment agent is not critical, it is generally in the range of 0.05 to 5 weight% with respect to the alumina micropowder (B).

[0012]

The component (B) content is 50 to 400 weight parts, preferably 80 to 350 weight parts, and more preferably 100 to 300 weight parts per 100 weight parts component (A). An adequate thermal conductivity cannot be imparted to the silicone rubber at contents below the lower limit on the aforementioned range, while exceeding the upper limit on this range causes an excessive increase in the viscosity of the inventive composition and thus impairs the workability. The addition of 180 to 400 weight parts component (B) per 100 weight parts component (A) is preferred in particular when the thermal conductivity of the inventive composition is to be brought to  $\geq 0.5$  W/(m·K).

[0013]

The iron oxide micropowder (C) functions to improve the strength and adhesive strength and hardness stability under heating of the cured material afforded by the inventive composition. The shape of component (C) is not critical and this component may be spherical, acicular, rhombic, dice shaped, or irregular.

[0014]

The average particle size of component (C) is in the range from 0.01 to 0.5  $\mu\text{m}$  and preferably is in the range from 0.1 to 0.4  $\mu\text{m}$ . A worsening of the workability occurs at below the lower limit on the aforementioned range, while component (C) undergoes sedimentation during long-term storage of the inventive composition when the upper limit on the aforementioned range is

exceeded. Two or more components (C) with different average particle sizes can be combined. The iron oxide may be, for example, ferric oxide (iron oxide red) or ferrosferric oxide (iron oxide black). The surface of component (C) can also be treated with a surface treatment agent as described above. This surface treatment may be carried out by the same procedures as described above.

[0015]

The component (C) content is 20 to 100 weight parts and preferably 20 to 50 weight parts per 100 weight parts component (A). The adhesive strength and hardness stability under heating of the cured material afforded by the inventive composition are inadequate below the aforementioned range. Exceeding the upper limit on the aforementioned range results in a substantial increase in the pre-cure viscosity of the inventive composition and in a loss of processability.

[0016]

The iron oxide micropowder (C), considered from the viewpoints of handling characteristics and dispersibility, is preferably a paste afforded by preliminary microdispersion in a portion of component (A). The component (C) content in the paste is not critical, but is preferably in the range of 10 to 80 weight% based on a consideration of the handling characteristics. This paste is readily prepared by adding component (C) to a prescribed quantity of component (A) and producing a uniform microdispersion using, for example, a three-roll mill.

[0017]

Component (D), which is cerium oxide micropowder, cerium hydroxide micropowder, or cerium-containing heteroorganosiloxane, interacts synergistically with component (C) to improve the adhesive strength and hardness stability under heating of the cured material afforded by the inventive composition. At a component (D) content below 0.1 part the adhesive strength and hardness stability under heating of the cured material from the inventive composition will not necessarily evidence improvement. Additions in excess of 2.0 weight parts afford no additional property improvements, and the range of 0.1 to 2.0 weight parts per 100 weight parts component (A) is therefore preferred for economic reasons.

[0018]

The cerium oxide micropowder and cerium hydroxide micropowder preferably have an average particle size of 0.01 to 10  $\mu\text{m}$ . Considered from the viewpoints of handling characteristics and dispersibility, the cerium oxide micropowder or cerium hydroxide micropowder preferably takes the form of a paste afforded by preliminary microdispersion in a portion of component (A). The component (D) content in the paste is not critical, but is preferably in the range of 10 to 80 weight% based on a consideration of the handling characteristics. This paste is readily prepared by adding component (D) to a prescribed quantity of component (A) and producing a uniform microdispersion using, for example, a three-roll mill.

[0019]

The cerium-containing heteroorganosiloxane is organosiloxane that contains at least one unit in which a cerium atom is bonded through an oxygen atom to a silicon atom. This

organosiloxane is preferably an oligomer. The silicon-bonded organic groups are preferably the same monovalent hydrocarbon as defined for R in component (A). This cerium-containing heteroorganosiloxane may be, for example, the reaction product of a cerium organocarboxylate salt and an organosiloxane unit-containing alkali metal silanolate, as described in Japanese Examined Patent Application Number (hereinafter referred to as Kokoku) Sho 61-24377 (24,377/1986); or the reaction product of cerium chloride and organosiloxane unit-containing alkali metal silanolate, as described in Kokoku Sho 53-980 (980/1978); or the composition afforded by adding an organocarboxylate salt or alkoxy compound of titanium to the reaction product of a cerium organocarboxylate salt and an alkali metal silanolate, as described in Kokoku Sho 53-12541 (12,541/1978).

[0020]

Among the preceding possibilities, cerium oxide micropowder is preferred for its ease of acquisition and cost advantages and because it has little influence on the viscosity of the composition according to the present invention.

[0021]

Component (E) is diorganopolysiloxane that contains at least two silicon-bonded hydrogen atoms in each molecule. This component induces cure of the inventive composition. The molecular structure of component (E) is not critical, and component (E) can have, for example, a straight chain, partially branched straight chain, branched chain, or cyclic molecular structure, wherein straight chain and partially branched straight chain molecular structures are particularly preferred. The viscosity of component (E) is also not specifically restricted and, for example, a viscosity at 25°C in the range of 3 to 10,000 centipoise is preferred and a viscosity at 25°C in the range of 3 to 300 centipoise is more preferred. The bonding position of the silicon-bonded hydrogen atoms in component (E) is also not critical, and the silicon-bonded hydrogen atom may be bonded in molecular chain terminal or pendant position. The non-hydrogen silicon-bonded groups in component (E) may be exemplified by alkyl groups such as methyl, ethyl, and propyl; aryl groups such as phenyl, tolyl, and xylyl; aralkyl groups such as benzyl and phenethyl; and halogenated alkyl groups such as 3-chloropropyl and 3,3,3-trifluoropropyl. Methyl is particularly preferred among the preceding. When component (A) contains two silicon-bonded alkenyl in each molecule, component (E) must contain at least three silicon-bonded hydrogen atoms in each molecule.

[0022]

Component (E) may be exemplified by the following:

- dimethylhydrogensiloxy-endblocked dimethylpolysiloxanes;
- dimethylhydrogensiloxy-endblocked methylhydrogenpolysiloxanes;
- dimethylhydrogensiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymers;
- trimethylsiloxy-endblocked methylhydrogenpolysiloxanes;
- trimethylsiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymers;
- silanol-endblocked methylhydrogenpolysiloxanes;
- silanol-endblocked dimethylsiloxane-methylhydrogensiloxane copolymers;



organopolysiloxanes comprising the  $(\text{CH}_3)_3\text{SiO}_{1/2}$  siloxane unit,  $(\text{CH}_3)_2\text{HSiO}_{1/2}$  siloxane unit, and  $\text{SiO}_{4/2}$  siloxane unit;  
organopolysiloxane comprising the  $(\text{CH}_3)_2\text{HSiO}_{1/2}$  siloxane unit and  $\text{SiO}_{4/2}$  siloxane unit;  
organopolysiloxanes comprising the  $(\text{CH}_3)\text{HSiO}_{2/2}$  siloxane unit,  $\text{CH}_3\text{SiO}_{3/2}$  siloxane unit, and  $\text{HSiO}_{3/2}$  siloxane unit;  
organopolysiloxane as afforded by replacing a portion of the methyl in the preceding organopolysiloxanes with phenyl, 3,3,3-trifluoropropyl, etc.; and  
mixtures of two or more of the preceding organopolysiloxanes.

[0023]

Component (E) is added in a quantity that affords from 0.3 to 5 moles silicon-bonded hydrogen atom in this component per 1 mole alkenyl in component (A) and preferably from 0.5 to 3 moles silicon-bonded hydrogen atom in this component per 1 mole alkenyl in component (A). The crosslink density is too low at below the lower limit on the aforementioned range, which can have a negative influence on the heat resistance of the cured silicone rubber. A dehydrogenation reaction is produced when the upper limit on the aforementioned range is exceeded, which can create the problem of hydrogen bubble formation and can have a negative influence on the heat resistance.

[0024]

The platinum catalyst (F) is a catalyst that accelerates cure of the composition according to the present invention, and in general those compounds known as catalysts of the hydrosilylation reaction may be used. This component may be exemplified by finely divided platinum, chloroplatinic acid, alcohol modifications of chloroplatinic acid, chelate compounds of platinum, platinum/diketone complexes, chloroplatinic acid/olefin coordination compounds, chloroplatinic acid/alkenylsiloxane complexes, and the preceding supported on a carrier such as alumina, silica, and carbon black. Chloroplatinic acid/alkenylsiloxane complexes are preferred among the preceding for their high activity as hydrosilylation catalysts. The platinum/alkenylsiloxane complexes disclosed in Kokoku Sho 42-22924 (22,924/1967) are particularly preferred. Also usable are finely divided spherical catalysts composed of thermoplastic resin containing at least 0.01 weight% (as platinum metal atoms) platinum catalyst. Component (F) is added to the inventive composition in a catalytic quantity, and an addition sufficient to induce cure of the inventive composition is satisfactory. In general, however, this component is added at preferably 0.01 to 500 weight parts as platinum metal per 1,000,000 weight parts component (A) and particularly preferably at 1 to 50 weight parts as platinum metal per 1,000,000 weight parts component (A).

[0025]

The composition according to this invention is obtained by intermixing the above-described components (A) to (F) to homogeneity. However, in addition to these components, the composition may contain, insofar as the object of this invention is not impaired, the various additives known for addition to silicone rubber compositions. These additives may be exemplified by pigments, flame retardants, internal release agents, electroconductive fillers for elimination of static, extender fillers, plasticizers, etc. A cure inhibitor is preferably added in

order to improve the handling characteristics and storage stability of the composition of the present invention. This cure inhibitor may be, for example, an acetylenic compound such as 2-methyl-3-butyne-2-ol, 2-phenyl-3-butyne-2-ol, 3,5-dimethyl-1-hexyne-3-ol, 1-ethynyl-1-cyclohexanol, 1,5-hexadiyne, and 1,6-heptadiyne; en-yne compounds such as 3,5-dimethyl-1-hexene-1-yne, 3-ethyl-3-buten-1-yne, and 3-phenyl-3-buten-1-yne; alkenylsiloxane oligomers such as 1,3-divinyltetramethyldisiloxane, 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane, and 1,3-divinyl-1,3-diphenyldimethyldisiloxane; ethynyl-functional silicon compounds such as methyltris(3-methyl-1-butyne-3-oxy)silane; nitrogenous compounds such as tributylamine, tetramethylethylenediamine, and benzotriazole; phosphorus-containing compounds such as triphenylphosphine; as well as sulfur-containing compounds, hydroperoxy compounds, hydrazines, and maleic acid derivatives. The content of these cure inhibitors is preferably in the range of 0.001 to 5 weight parts per 100 weight parts component (A).

[0026]

A microparticulate reinforcing silica with a specific surface area of at least  $50 \text{ m}^2/\text{g}$  may be added in order to obtain additional improvements in the strength of the cured material afforded by the inventive composition. Within the sphere of hydrophilic silicas, this reinforcing silica may be specifically exemplified by dry-method silicas such as Aerosil 50, 130, 200, and 300 (products of Nippon Aerosil Co., Ltd., and Degussa AG), Cab-o-Sil MS-5, MS-7, and MS-75 (products of Cabot Corporation), and Rheorosil QS-102 and QS-103 (products of Tokuyama Corporation), and by wet-method silicas such as Nipsil LP (product of Nippon Silica Industrial Co., Ltd.). With regard to hydrophobic silicas as afforded by surface treatment of the aforementioned hydrophilic silicas, this reinforcing silica may be exemplified by Aerosil R-812, R-812S, R-972, and R-974 (products of Degussa AG), Rheorosil MT-10 (product of Tokuyama Corporation), and the Nipsil SS series (products of Nippon Silica Industrial Co., Ltd.). These microparticulate reinforcing silicas are preferably added at 0.1 to 80 weight parts per 100 weight parts component (A), more preferably at 5 to 50 weight parts per 100 weight parts component (A), and most preferably at 5 to 10 weight parts per 100 weight parts component (A).

[0027]

An SiH-free organopolysiloxane resin may be used for the same purpose. This SiH-free organopolysiloxane resin may be exemplified by

organopolysiloxane comprising the  $(\text{CH}_3)_3\text{SiO}_{1/2}$  siloxane unit and  $\text{SiO}_{4/2}$  siloxane unit;

organopolysiloxane comprising the  $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$  siloxane unit,  $(\text{CH}_3)_3\text{SiO}_{1/2}$  siloxane unit, and  $\text{SiO}_{4/2}$  siloxane unit; and

organopolysiloxane comprising the  $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$  siloxane unit,  $(\text{CH}_3)_3\text{SiO}_{1/2}$  siloxane unit, and  $\text{SiO}_{3/2}$  siloxane unit.

The content of this organopolysiloxane resin preferably is 0.1 to 80 weight parts per 100 weight parts component (A) and more preferably is 1 to 50 weight parts per 100 weight parts component (A).

[0028]

The thermoconductive addition-curable liquid silicone rubber composition according to this invention may be prepared by intermixing components (A) to (F) and any of the above-described optional components to homogeneity using a known mixing/kneading means such as a two-roll mill, Banbury mixer, kneader mixer, planetary mixer, Ross mixer, Hobart mixer, etc. In order to improve the storage stability at around room temperature and maintain an excellent post-storage curability in such applications as co-molding, the composition according to this invention is preferably formulated as a two-package silicone rubber composition divided into a composition containing at least components (A) and (F) but not containing component (E) and a composition containing at least components (A) and (E) but not containing component (F).

[0029]

The inventive thermoconductive addition-curable liquid silicone rubber composition obtained as described above may be molded as desired by known molding methods. The inventive composition can in particular be cured by, for example, press molding, extrusion molding, transfer molding, injection molding, calender molding, and coating molding, and may be processed not just into sheet but also into moldings with various shapes. In addition, unified composites with a variety of substrates may be readily prepared by curing the inventive composition while in contact with a substrate such as primer-coated metal. The molding temperature is generally at least 80°C and is preferably in the range from 100 to 180°C. The addition curing reaction in hydrosilylation-based silicone rubbers will proceed even below the lower limit on the aforementioned temperature range, but the use of such temperatures can require long molding times and can result in the failure to obtain an acceptable adhesive strength in the fabrication of a composite article through adherence to another article. A post-vulcanization for several hours at 150 to 300°C is preferably implemented in order to stabilize the post-cure physical properties.

[0030]

The composition according to the present invention has a thermal conductivity of at least 0.3 W/(m·K). The thermal conductivity may be readily measured using, for example, a QTM-500 Quick Thermal Conductivity Meter from Kyoto Electronics Manufacturing Co., Ltd.

[0031]

Surface treatment of the surface of the alumina micropowder (B) with, for example, organoalkoxysilane or tetraalkoxysilane or its partial hydrolysis and condensation product can improve the handling characteristics by reducing the viscosity of the inventive composition and can improve the storage stability by preventing sedimentation of the alumina micropowder (B).

[0032]

In addition, the handling characteristics of component (C) and its dispersibility in component (A) are improved when the iron oxide micropowder (C) takes the form of a paste afforded by preliminary microdispersion in a portion of the diorganopolysiloxane (A).

[0033]

**Examples**

The thermoconductive addition-curable liquid silicone rubber composition according to the present invention is described in greater detail hereinbelow by working examples. Parts in the examples denotes weight parts, while % denotes weight%. The values reported for viscosity were measured at 25°C. The viscosity values reported for the compositions prepared in the working and comparative examples were measured at 25°C using a BH rotary viscometer (rotor no. 7, 10 rpm) from Tokyo Keiki Co., Ltd.

[0034]

**Method for measuring the hardness**

The hardness measurement test specimen (thickness = 6 mm) was prepared by press-molding the inventive composition for 10 minutes at 120°C (clamping pressure = 50 tons) and then holding for 4 hours in a convection oven at 200°C. The hardness of the test specimen was measured according to JIS K 6249. In addition, in order to measure the change in hardness, a test specimen whose hardness had been measured in this manner was placed in a 230°C oven, withdrawn after the specified time, and submitted to hardness measurement as before.

[0035]

**Method for measuring the initial physical properties**

The other initial physical properties were measured as follows. The silicone rubber test specimen (thickness = 2 mm) for physical property measurement was prepared by press-molding the inventive composition for 10 minutes at 120°C (clamping pressure = 50 tons) and then holding for 4 hours in a convection oven at 200°C. The tensile strength and elongation of the test specimen were measured according to JIS K 6249. For the compression set and rebound resilience, a test specimen according to JIS K 6249 was fabricated using the conditions reported above and the compression set was measured by the method described in JIS K 6249 and the rebound resilience was measured by the method described in JIS K 6255.

[0036]

**Method for measuring the thermal conductivity**

The silicone rubber test specimen (thickness = 12 mm) for measurement of the thermal conductivity was prepared by press-molding the inventive composition for 10 minutes at 120°C (clamping pressure = 50 tons) and then holding for 4 hours in a convection oven at 200°C. The thermal conductivity of the resulting test specimen was measured using a QTM-500 Quick Thermal Conductivity Meter from Kyoto Electronics Manufacturing Co., Ltd.

[0037]

**Procedure for evaluating the strength and adherence of an aluminum panel composite**

A commercially available silane primer (DY39-067 from Dow Corning Toray Silicone Co., Ltd.) was uniformly coated on the surface of an aluminum test panel (A5052P, 7.5 cm × 2.5 cm × 1 mm, from Kabushiki Kaisha PALTEC) and was dried for 60 minutes at 25°C and 60% relative humidity. After this test panel had been installed in a mold cavity, the inventive composition was poured in and an aluminum panel composite test specimen was fabricated by press-molding for 10 minutes at 120°C (clamping pressure = 50 tons) and then holding for 4 hours in a

convection oven at 200°C. A silicone rubber layer with a thickness of 5 mm was formed on the aluminum panel composite test specimen.

[0038]

Incisions (2 mm width  $\times$  1.25 cm length  $\times$  5 mm depth) were introduced with a cutter into the silicone rubber layer on this test specimen and the silicone rubber layer on the aluminum panel was divided into 60 rubber sections. Each rubber section was connected to a tensile tester (Autograph AGC-50D from Shimadzu) and a 90° peel test was carried out at a speed of 50 mm/minute. During this test, the force required to separate the rubber sections and the aluminum panel was recorded in order to measure the rupture strength of the test specimen. The adherence was also evaluated by inspecting the cohesive failure ratio of the rupture surface. The load required for rubber section separation was divided by the rubber section width to give the rupture strength value.

[0039]

An aluminum panel composite test specimen as described above was also introduced into a 230°C oven and was thermally aged for the specified time period. The rupture strength and adherence of the test specimen were then evaluated as described above.

[0040]

#### **Evaluation of the adherence to fluororesin**

A fluororesin (PFA) tube whose interior surface had been subjected to a chemical etch with a sodium metal/liquid ammonia solution was cut into a strip (4.0 cm  $\times$  7.0 cm). A commercially available silane primer (DY39-067 from Dow Corning Toray Silicone Co., Ltd.) was uniformly coated on the side corresponding to the tube interior and was dried for 60 minutes at 25°C and 60% relative humidity. This was installed in a mold cavity in such a manner that the primer-treated surface was the upper surface, the inventive composition was poured in, and a silicone rubber layer with a thickness of about 6 mm was formed by press-molding for 10 minutes at 120°C and then holding for 4 hours in a convection oven at 200°C.

[0041]

The resulting adhesion test specimen was cut into a strip (length 4.0 cm  $\times$  width 1.0 cm  $\times$  thickness 0.6 cm) and a 180° peel test was carried out at a speed of 50 mm/minute. The adherence was evaluated by inspecting the cohesive failure ratio of the adhesion rupture surface.

[0042]

An adhesion test specimen as described above was also introduced into a 230°C oven and was thermally aged for the specified time period. The adherence was then evaluated as described above.

[0043]

#### **Evaluation of roll durability**

A commercially available silane primer (DY39-067 from Dow Corning Toray Silicone Co., Ltd.) was coated on an aluminum core (diameter 80 mm  $\times$  length 400 mm) and was dried for 60 minutes at 25°C and 60% relative humidity. The inventive silicone rubber composition was then

coated on the cylinder followed by curing by heating for 30 minutes at 150°C and secondary curing for 4 hours at 200°C to give a 6 mm-thick silicone rubber layer on the aluminum core. The surface of this silicone rubber layer was spray coated with a primer (GLS-103SR from Daikin Industries, Ltd.) for fluororubbers and, after drying for 10 minutes at 50°C, a fluororubber latex (Dai-El Latex GLS-213 from Daikin Industries, Ltd.) was applied by spray coating. Baking for 30 minutes at 320°C then gave a silicone rubber-coated roll having a fluororubber surface layer.

[0044]

Rolls fabricated as described above were installed as the fixing rolls in a plain paper copier. A roll durability evaluation test was carried out by passing 60 sheets of white paper per minute between the fixing rolls while applying a nip load of 2450 N and using a heater temperature in the fixing section of 190°C.

[0045]

Reference Example 1

[Preparation of iron oxide-containing diorganopolysiloxane paste]

40 parts iron oxide micropowder (average particle size = 0.17  $\mu\text{m}$ , Bayferrox 130M from Bayer AG) were blended and uniformly mixed into 60 parts dimethylvinylsiloxyl-endblocked dimethylpolysiloxane (viscosity = 10,000 mPa·s, vinyl content = 0.13 weight%). Passage 3 times through a three-roll mill then gave the iron oxide-containing diorganopolysiloxane paste.

[0046]

Example 1

The following were introduced into a Ross mixer: 40 parts trimethylsiloxyl-endblocked dimethylsiloxane-methylvinylsiloxane copolymer (viscosity = 7,000 mPa·s, vinyl content = 0.30 weight%), 280 parts alumina micropowder with an average particle size of 2.0  $\mu\text{m}$  (Alumina AL-43ME from Showa Denko Kabushiki Kaisha), 100 parts of the iron oxide-containing diorganopolysiloxane paste prepared in Reference Example 1, and 0.5 part tetra(n-propoxy)silane as surface treatment agent. After stirring at room temperature for 30 minutes, stirring was then carried out under reduced pressure for 90 minutes with heating at 170°C. After cooling to room temperature, the following were introduced with mixing to homogeneity:

3.3 parts dimethylhydrogensiloxyl-endblocked dimethylpolysiloxane (viscosity = 10 mPa·s, silicon-bonded hydrogen atom content = 0.16 weight%, this quantity of addition gave 0.5 mole silicon-bonded hydrogen atom in this dimethylhydrogensiloxyl-endblocked dimethylpolysiloxane per 1 mole vinyl in the aforementioned dimethylsiloxane-methylvinylsiloxane copolymer),

0.73 part trimethylsiloxyl-endblocked dimethylsiloxane-methylhydrogensiloxane copolymer (viscosity = 5 mPa·s, silicon-bonded hydrogen atom content = 0.75 weight%, this quantity of addition gave 0.5 mole silicon-bonded hydrogen atom in this dimethylsiloxane-methylhydrogensiloxane copolymer per 1 mole vinyl in the aforementioned dimethylsiloxane-methylvinylsiloxane copolymer),

0.25 part cerium oxide micropowder (high-purity cerium oxide from Anan Kasei Co., Ltd.), and

0.15 part 3,5-dimethyl-1-hexyn-3-ol as cure inhibitor.

This was followed by the introduction with mixing to homogeneity of 0.5 part isopropanolic chloroplatinic acid solution (platinum metal content = 5 weight%) to give a thermoconductive addition-curable liquid silicone rubber composition. The viscosity of the resulting composition was 100 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0047]

#### Example 2

A thermoconductive addition-curable liquid silicone rubber composition was prepared as in Example 1, but in this example using 295 parts of the alumina micropowder and 63 parts of the iron oxide-containing diorganopolysiloxane paste prepared in Reference Example 1 and also adding 22 parts of the dimethylvinylsiloxane-endblocked dimethylpolysiloxane (viscosity = 10,000 mPa·s, vinyl content = 0.13 weight%) used in Reference Example 1. The viscosity of the resulting composition was 100 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0048]

#### Example 3

A thermoconductive addition-curable liquid silicone rubber composition was prepared as in Example 1, but in this example adding 5 parts hydrophobic dry-method silica (Rheorosil DM30, surface treated with dimethyldichlorosilane, product of Tokuyama Corporation) at the same time as the alumina micropowder. The viscosity of the resulting composition was 180 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0049]

#### Example 4

The following were introduced into a Ross mixer: 40 parts trimethylsiloxane-endblocked dimethylsiloxane-methylvinylsiloxane copolymer (viscosity = 7,000 mPa·s, vinyl content = 0.30 weight%), 280 parts alumina micropowder with an average particle size of 2.0  $\mu\text{m}$  (Alumina AL-43ME from Showa Denko Kabushiki Kaisha), 100 parts of the iron oxide-containing diorganopolysiloxane paste prepared in Reference Example 1, 0.5 part tetra(n-propoxy)silane as surface treatment agent, and 5 parts organopolysiloxane resin with the formula



(vinyl content = 0.8%,  $n$  is a number that provides a value of 4,600 for the number-average molecular weight of this organopolysiloxane). After stirring at room temperature for 30 minutes,

stirring was then carried out under reduced pressure for 90 minutes with heating at 170°C. After cooling to room temperature, the following were introduced with mixing to homogeneity:

- 4.5 parts dimethylhydrogensiloxy-endblocked dimethylpolysiloxane (viscosity = 10 mPa·s, silicon-bonded hydrogen atom content = 0.16 weight%, this quantity of addition gave 0.5 mole silicon-bonded hydrogen atom in this dimethylhydrogensiloxy-endblocked dimethylpolysiloxane per 1 mole vinyl in the aforementioned dimethylsiloxane-methylvinylsiloxane copolymer),
- 1.0 part trimethylsiloxy-endblocked dimethylsiloxane-methylhydrogensiloxane copolymer (viscosity = 5 mPa·s, silicon-bonded hydrogen atom content = 0.75 weight%, this quantity of addition gave 0.5 mole silicon-bonded hydrogen atom in this dimethylsiloxane-methylhydrogensiloxane copolymer per 1 mole vinyl in the aforementioned dimethylsiloxane-methylvinylsiloxane copolymer),
- 0.25 part cerium oxide micropowder (high-purity cerium oxide from Anan Kasei Co., Ltd.), and
- 0.15 part 3,5-dimethyl-1-hexyn-3-ol as cure inhibitor.

This was followed by the introduction with mixing to homogeneity of 0.5 part isopropanolic chloroplatinic acid solution (platinum metal content = 5 weight%) to give a thermoconductive addition-curable liquid silicone rubber composition. The viscosity of the resulting composition was 120 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0050]

#### Comparative Example 1

A thermoconductive addition-curable liquid silicone rubber composition was prepared as in Example 1, but in this case using 38 parts of the iron oxide-containing diorganopolysiloxane paste prepared in Reference Example 1, changing the alumina micropowder addition to 305 parts, and also adding 38 parts of the dimethylvinylsiloxy-endblocked dimethylpolysiloxane (viscosity = 10,000 mPa·s, vinyl content = 0.13 weight%) used in Reference Example 1. The viscosity of the resulting composition was 100 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0051]

#### Comparative Example 2

A thermoconductive addition-curable liquid silicone rubber composition was prepared as in Example 1, but in this case using 60 parts dimethylvinylsiloxy-endblocked dimethylpolysiloxane (viscosity = 10,000 mPa·s, vinyl content = 0.13 weight%) in place of the iron oxide-containing diorganopolysiloxane paste and changing the alumina micropowder addition to 320 parts. The viscosity of the resulting composition was 90 Pa·s.



This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0052]

#### Comparative Example 3

A thermoconductive addition-curable liquid silicone rubber composition was prepared as in Comparative Example 2, but in this case without the addition of the cerium oxide micropowder. The viscosity of the resulting composition was 90 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0053]

#### Comparative Example 4

A thermoconductive addition-curable liquid silicone rubber composition was prepared as in Example 1, but in this case without the addition of the cerium oxide micropowder. The viscosity of the resulting composition was 90 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0054]

#### Comparative Example 5

A thermoconductive addition-curable liquid silicone rubber composition was prepared as in Example 1, but in this case adding 140 parts quartz micropowder (Crystallite VX-S2 from Kabushiki Kaisha Tatsumori) in place of the alumina micropowder. The viscosity of the resulting composition was 90 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0055]

#### Comparative Example 6

A thermoconductive addition-curable liquid silicone rubber composition was prepared as in Comparative Example 2, but in this case adding 310 parts of the alumina micropowder and adding 10 parts hydrophobic dry-method silica (Rheorosil DM30, surface treated with dimethyldichlorosilane, product of Tokuyama Corporation) at the same time as the alumina micropowder. The viscosity of the resulting composition was 280 Pa·s.

This composition was submitted to measurement by the methods described above of the hardness, initial physical properties, rupture strength and adherence of the aluminum panel composite, adherence to fluororesin, and properties after thermal ageing at 230°C. The results are reported in Tables 2 to 6.

[0056]

Table 1 reports the quantities of addition for each component for the compositions in Examples 1 to 4 and Comparative Examples 1 to 6.

Table 1.

	Example 1	Example 2	Example 3	Example 4
component (A)-1	60	60	60	60
component (A)-2	40	40	40	40
component (B)	280	295	280	280
component (C)	40	25	40	40
reinforcing silica	—	—	5	—
silicone resin	—	—	—	5
component (D)	0.25	0.25	0.25	0.25
component (E)-1	3.3	3.3	3.3	4.5
component (E)-2	0.73	0.73	0.73	1
component (F)	0.5	0.5	0.5	0.5
surface treatment agent	0.5	0.5	0.5	0.5
extender filler	—	—	—	—
cure inhibitor	0.15	0.15	0.15	0.15

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
component (A)-1	60	60	60	60	60	60
component (A)-2	40	40	40	40	40	40
component (B)	305	320	280	320	—	310
component (C)	15	—	40	—	40	—
reinforcing silica	—	—	—	—	—	10
silicone resin	—	—	—	—	—	—
component (D)	0.25	0.25	—	—	0.25	0.25
component (E)-1	3.3	3.3	3.3	3.3	3.3	3.3
component (E)-2	0.73	0.73	0.73	0.73	0.73	0.73
component (F)	0.5	0.5	0.5	0.5	0.5	0.5
surface treatment agent	0.5	0.5	0.5	0.5	0.5	0.5
extender filler	—	—	—	—	140	—
cure inhibitor	0.15	0.15	0.15	0.15	0.15	0.15

- component (A)-1: dimethylvinylsiloxo-*endblocked* dimethylpolysiloxane with a viscosity of 10,000 mPa·s and a vinyl content of 0.13%
- component (A)-2: trimethylsiloxo-*endblocked* dimethylsiloxane-methylvinylsiloxane copolymer with a viscosity of 7,000 mPa·s and a vinyl content of 0.30%
- component (B): alumina micropowder with an average particle size of 2.0  $\mu\text{m}$  (Alumina AL-43ME from Showa Denko Kabushiki Kaisha)
- component (C): iron oxide micropowder with an average particle size of 0.17  $\mu\text{m}$  (Bayferrox 130M from Bayer AG)
- component (D): cerium oxide micropowder (high-purity cerium oxide from Anan Kasei Co., Ltd.)
- component (E)-1: dimethylhydrogensiloxo-*endblocked* dimethylpolysiloxane (viscosity = 10 mPa·s, silicon-bonded hydrogen atom content = 0.16 weight%)
- component (E)-2: trimethylsiloxo-*endblocked* dimethylsiloxane-methylhydrogensiloxane copolymer (viscosity = 5 mPa·s, silicon-bonded hydrogen atom content = 0.75%)
- component (F): isopropanolic chloroplatinic acid solution (platinum metal content = 5%)
- surface treatment agent: tetra(n-propoxy)silane
- extender filler: quartz micropowder with an average particle size of 5  $\mu\text{m}$  (Crystallite VX-S2 from Kabushiki Kaisha Tatsumori)
- cure inhibitor: 3,5-dimethyl-1-hexyn-3-ol

[0057]

Table 2. Initial physical properties

	unit	Ex. 1	Ex. 2	Ex. 3	Ex. 4
specific gravity	—	2.25	2.24	2.25	2.25
hardness (JIS type A)	—	57	57	60	61
tensile strength (pattern no. 3)	MPa	4.0	3.9	4.8	4.7
elongation (pattern no. 3)	%	200	190	180	170
rebound resilience	%	58	58	55	55
thermal conductivity	W/m·K	1.0	1.0	1.0	1.0
compression set (180°C/22 hr 25% compression)	%	11	12	15	15

	unit	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
specific gravity	—	2.24	2.23	2.25	2.23	1.67	2.23
hardness (JIS type A)	—	57	57	57	57	58	63
tensile strength (pattern no. 3)	MPa	3.7	3.6	4.2	3.6	3.8	2.9
elongation (pattern no. 3)	%	220	220	190	220	190	170
rebound resilience	%	59	60	58	60	55	50
thermal conductivity	W/m·K	1.0	1.0	1.0	1.0	0.6	1.0
compression set (180°C/22 hr 25% compression)	%	12	10	12	12	8	20

[0058]

Table 3. Change in hardness (thermal ageing at 230°C)

	initial	after hours 170	after hours 220	after hours 310	after hours 480
Example 1	57	57	57	57	58
Example 2	57	57	57	58	58
Example 3	60	60	60	61	61
Example 4	61	61	61	61	62
Comp. Ex. 1	57	53	53	54	55
Comp. Ex. 2	57	51	52	53	57
Comp. Ex. 3	57	53	53	53	55
Comp. Ex. 4	56	47	52	57	61
Comp. Ex. 5	58	54	52	52	52
Comp. Ex. 6	63	53	55	56	58

(JIS type A hardness, test specimen thickness: 6 mm)

[0059]

Table 4. Rupture strength of aluminum panel composite test specimens

	initial	after hours 170	after hours 220	after hours 310	after hours 480
Example 1	2.1	2.1	2.3	2.0	2.0
Example 2	2.0	2.0	2.0	1.9	2.0
Example 3	2.5	2.5	2.7	2.3	2.4
Example 4	2.5	2.5	2.6	2.4	2.4
Comp. Ex. 1	1.7	1.7	1.6	1.5	1.3
Comp. Ex. 2	1.6	1.7	1.6	1.5	1.2
Comp. Ex. 3	1.7	1.8	1.8	1.7	1.7
Comp. Ex. 4	0.8	1.7	1.7	1.2	1.4
Comp. Ex. 5	1.6	1.7	1.6	1.2	1.2
Comp. Ex. 6	0.8	1.7	1.6	1.4	1.2

(strength unit: N/mm)

[0060]

Table 5. Adherence to aluminum panel (cohesive failure ratio)

	initial	after 170 hours	after 220 hours	after 310 hours	after 480 hours
Example 1	○	○	○	○	○
Example 2	○	○	○	○	○
Example 3	○	○	○	○	○
Example 4	○	○	○	○	○
Comp. Ex. 1	○	Δ	Δ	Δ	Δ
Comp. Ex. 2	Δ	Δ	Δ	×	×
Comp. Ex. 3	Δ	○	Δ	Δ	Δ
Comp. Ex. 4	Δ	Δ	Δ	×	×
Comp. Ex. 5	Δ	Δ	Δ	×	×
Comp. Ex. 6	Δ	○	Δ	×	×

cohesive failure ratio:    ○ :    ≥ 90%  
                                      Δ :    50-89%  
                                      × :    ≤ 49%

[0061]

Table 6. Adherence to fluororesin (cohesive failure ratio)

	initial	after 170 hours	after 220 hours	after 310 hours	after 480 hours
Example 1	○	○	○	○	○
Example 2	○	○	○	○	○
Example 3	○	○	○	○	○
Example 4	○	○	○	○	○
Comp. Ex. 1	○	Δ	Δ	×	×
Comp. Ex. 2	Δ	Δ	×	×	×
Comp. Ex. 3	○	○	○	Δ	Δ
Comp. Ex. 4	Δ	×	×	×	×
Comp. Ex. 5	×	×	Δ	Δ	×
Comp. Ex. 6	Δ	○	×	×	×

cohesive failure ratio:    ○ :    ≥ 90%  
                                      Δ :    50-89%  
                                      × :    ≤ 49%

[0062]

## Example 5

Silicone rubber-covered rolls were fabricated using the silicone rubber composition of Example 1. These rolls were submitted to roll durability evaluation testing with the following results: at least 300,000 sheets could be transported through unproblematically and no abnormality whatever was observed in the rolls themselves.

[0063]

## Example 6

Roll durability evaluation testing was carried out as in Example 5, but in this case using the silicone rubber composition of Example 2. At least 300,000 sheets could be transported through unproblematically and no abnormality whatever was observed in the rolls themselves.

[0064]

Example 7

Roll durability evaluation testing was carried out as in Example 5, but in this case using the silicone rubber composition of Example 3. At least 300,000 sheets could be transported through unproblematically and no abnormality whatever was observed in the rolls themselves.

[0065]

Example 8

Roll durability evaluation testing was carried out as in Example 5, but in this case using the silicone rubber composition of Example 4. At least 300,000 sheets could be transported through unproblematically and no abnormality whatever was observed in the rolls themselves.

[0066]

Comparative Example 7

Roll durability evaluation testing was carried out as in Example 5, but in this case using the silicone rubber composition of Comparative Example 1. Paper creasing occurred at the 100,000th sheet. Inspection of the roll surface showed partial debonding of the fluororubber surface layer.

[0067]Comparative Example 8

Roll durability evaluation testing was carried out as in Example 5, but in this case using the silicone rubber composition of Comparative Example 2. A paper jam occurred at the 82,000th sheet. Inspection of the roll surface showed almost complete debonding of the fluororubber surface layer.

[0068]

Comparative Example 9

Roll durability evaluation testing was carried out as in Example 5, but in this case using the silicone rubber composition of Comparative Example 6. A paper jam occurred at the 60,000th sheet. Inspection of the roll surface showed almost complete debonding of the fluororubber surface layer and also revealed partial rupture of the silicone rubber layer with exposure of the aluminum core.

[0069]

Advantageous Effects of the Invention

As has been described in the preceding, the inventive thermoconductive addition-curable liquid silicone rubber composition, because it comprises components (A) to (F) and in particular because it contains the (B) alumina micropowder, (C) iron oxide micropowder, and (D) cerium oxide micropowder, cerium hydroxide micropowder, or cerium-containing heteroorganosiloxane, exhibits an excellent adherence to substrate in contact with the composition during its cure and cures to form silicone rubber that exhibits an excellent thermal conductivity and good strength

and that exhibits a very stable hardness even when exposed to long-term heating. Articles formed by the cure of this thermoconductive addition-curable liquid silicone rubber composition exhibit a high thermal conductivity and undergo little change in strength and physical properties even when subjected to long-term use under heating. The inventive thermoconductive addition-curable liquid silicone rubber composition can therefore be used with excellent advantage for the fixing rolls and belts in electrophotographic copiers, electronic printers, and facsimile machines. More particularly, due to the excellent adherence to metals and fluororesins and fluororubbers, the inventive thermoconductive addition-curable liquid silicone rubber composition is ideal for use as the silicone rubber in silicone rubber-covered heat fixing rolls in which a silicone rubber surface layer is covered by a fluororesin or fluororubber.



(Document Designation)      Abstract

[Abstract]

[Problem]

A thermoconductive liquid silicone rubber composition that exhibits excellent adherence to substrate in contact with the composition during its cure and that after curing exhibits a fully satisfactory strength and high thermal conductivity and does not exhibit changes in these properties even when subjected to long-term heating.

[Solution]

Thermoconductive addition-curable liquid silicone rubber composition having a thermal conductivity of at least  $0.3 \text{ W}/(\text{m}\cdot\text{K})$  after curing which comprises

- (A) 100 weight parts liquid diorganopolysiloxane that contains at least two silicon-bonded alkenyl groups in each molecule,
- (B) 50 to 400 weight parts alumina micropowder,
- (C) 20 to 100 weight parts iron oxide micropowder,
- (D) 0.1 to 2.0 weight parts cerium oxide micropowder, cerium hydroxide micropowder, or cerium-containing heteroorganosiloxane,
- (E) organopolysiloxane that contains at least two silicon-bonded hydrogen atoms in each molecule, and
- (F) platinum catalyst in a catalytic quantity.